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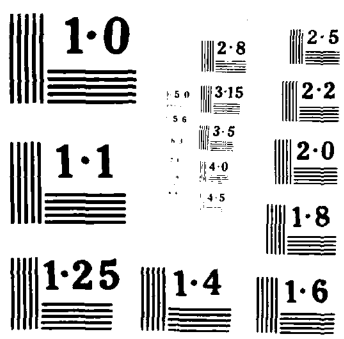
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DETERMINATION OF CHLORIDE IN HYDRAULIC FLUIDS

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In recent years, the adverse corrosion effects of chloride have become a great concern. Several analytical techniques have been reported in the literature for the determination of chloride in a variety of samples. The contamination of hydraulic fluids with seawater presents concern for the corrosion of an aircraft stationed on a carrier. An accurate, sensitive and a simple method, therefore, is required to monitor the chloride concentration and to assure proper function of the hydraulic system. In this report an improved ion selective electrode method for chloride in hydraulic fluids contaminated with seawater is presented.

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INTRODUCTION

The contamination of hydraulic fluids with seawater presents a concern about possible corrosion of the hydraulic system of an aircraft stationed on a carrier. It is desirable, therefore, to determine the concentration of free chloride ions in hydraulic fluids. Often the chloride concentration is very low (few parts per million, ppm), and is out of the sensitivity range of the standard methods.[1-4] The ion selective electrode, micro-coulometric titration and inductively coupled plasma-atomic emission methods have also been mentioned in the literature for the chloride determination.[5-8]

EPA approved gas chromatographic method with electron capture detector has been used for the analysis of hydraulic fluids contaminated with halogenated compounds such as freons and PCB's. A method using ion selective electrochemical sensors has been used successfully for seawater contaminated with halogenated fluids. In this method the sample is centrifuged with freon, the separated aqueous layer (approximately lml) is siphoned, diluted to a known volume and analyzed for the chloride. Chloride in a 5mg/L concentration can be determined quantitatively, however, at concentrations below lmg/L, the analysis is limited by the finite solubility of the ion electrode itself.

Some hydraulic fluids such as ethylene glycol contain mercaptobenzothiazol (1%) and triethanolamine phosphate (1%) as corrosion inhibitors, and other additives. These fluids cannot be analyzed by the conventional silver nitrate, O-toluidine, ion exchange methods, etc. The precipitation, extraction and distillation methods for the chloride determination are very time consuming. The extraction of the aqueous part of a hydraulic fluid is almost impossible due to the miscibility of ethyleme glycol with water and other organic solvents.

This work reports the utilization of 1 percent copper nitrate solution to precipitate mercaptobenzothiazole and triethanolamine phosphate from the hydraulic fluid samples and analyze the filtrate for total chloride ions using the ion selective electrode (ISE) method.

EXPERIMENTAL PROCEDURE

Apparatus

pH-meter or Ionalyzer (901, Orion)

Chloride electrode (94-17 Orion solid state or any other manufacturer)

Double junction reference electrode

Reagents and solutions

Sodium chloride

Sodium nitrate

Copper nitrate AR Grade

Mercaptobenzothiazol

Triethanolamine phosphate

Ethylene glycol, chromatoquality

The standard chloride stock solution (1000 mg/L) was prepared by dissolving sodium chloride in deionized distilled water. A 5M sodium nitrate solution was used as an ion strength adjustor (ISA). 1% solutions of mercaptobenzothiazol and triethanolamine phosphate used to simulate the sample matrix. Copper nitrate in 1, 2, 5, and 10 percent concentrations was used as the complexing agent to precipitate the interferents.

Procedure

After several unsuccessful trails of extraction with various solvents and reagents (nickel and iron solutions), an attempt was made to use copper solution to precipitate the interferents. Copper was selected due to its affinity for sulfur. Several experiments were performed with various concentrations of copper solutions added to the standard chloride solution and it was determined that a 1% copper solution in the presence of 1% acid and 2mI of ISA solution did not interfere with the chloride determination.

The copper nitrate solution was added to each of the following:

1. distilled water (blank)
2. distilled water, mercaptobenzothiazol (1% w/v), and triethanolamine phosphate (1% w/v).
3. ethylene glycol (blank, 10% v/v)
4. ethylene glycol (10% v/v), mercaptobenzothiazol (1% w/v), and triethanolamine phosphate (1% w/v)
5. standard chloride solutions in 1, 10, 100 and 1000 mg/L concentration
6. standard chloride solutions in 1, 10, 100, and 1000 mg/L, mercaptobenzothiazol (1% w/v), triethanolamine phosphate (1% w/v), and ethylene glycol (10% w/v)
7. sample solutions diluted ten times (3 sets of each sample)
8. undiluted samples

All the solutions (1-8) were stirred gently, the resulting percipitates were allowed to settle and then filtered off. The filtrates were treated again with a small amount of copper nitrate solution to make sure that precipitation was complete. The solid residues were washed, dried, and analyzed for their contents using infrared spectroscopy. The IR analysis proved the presence of mercaptobenzothiazol and triethanolamine phosphate in the residues. Two ml of ISA solution was added to all the filtrates before analysis, so that the background ionic strength remained high and constant relative to variable chloride concentrations.

Relative potential measurements were made on an Ionalyzer using a chloride ion selective electrode and a double junction saturated calomel electrode as the reference electrode. Calibration curves were prepared by measuring the potentials (millivolts) of standard chloride solution (1, 10, 100, and 1000 mg/L) and solution #5, and plotting the values on a semilog graph, Fig. 1. Potential values obtained for solution #6 were different than those obtained for solution #5. The precipitates from solutions 1 thru 8 were dissolved in a small amount of acid and analyzed for any chloride ions.

An attempt was also made to perform direct analyses of solutions #4, 6, 7, and 8. The precipitates were allowed to settle and then measurements were made in the supernatant liquid. Results were not encouraging to pursue the analysis.

RESULTS

A mathematical description of an electrode behavior is given by the Nernst equation

$$E = E_K + (2.3RT/nF)\log A$$

where,

E	=	potential in millivolts
E_K	=	constant that depends on reference electrode
$2.3RT/nF$	=	Nernst factor
R and F	=	constants
n	=	charge on the ion
T	=	temperature in Kelvin
A	=	activity of the ion to which electrode is responding

When n is 1, the Nernst factor at 25°C is equal to 59.16 mv and this value is temperature dependent. An electrode response of 59 mv is observed in a standard chloride calibration curve, Fig. 1. Data for the potential measurements of chloride in water and 10% (v/v) ethylene glycol is presented in Table

1. An average electrode response value of 54-55 mv obtained for the chloride measurements in ethylene glycol indicates that the electrode behavior is satisfactory, as shown in Fig. 1, curves 3 & 4.

Data for the effect of copper concentration on chloride measurements is presented in Tables 2 and 3. The electrode response for most of the copper additions in 1%, 2%, 5%, and 10% concentrations did not conform to the Nernst factor. Potential varied from 45-58 mv for every ten fold change in chloride concentration. A constant value of 56 mv was observed only between 10 and 100 mg/L chloride irrespective of the copper concentrations. The best results for chloride in ethlene glycol were obtained in the presence of 1% copper with 1% acid and 2mL ISA solutions.

The hydraulic fluid (MIL-H-5559) samples supposedly contaminated with seawater were analyzed by the addition of 1% copper, 1% acid, and 2mL of ISA solutions. Since the concentration of chloride found in the hydraulic fluid was low, the standard addition method was also used. Results are reported in Table 5. The chloride values obtained by the standard addition method confirm the direct analysis results. The tabulated data proves that chloride can be determined in the contaminated hydraulic fluids by this method.

CONCLUSION

The ion selective electrode method has many attractive features. The operation cost is low and a sample can be analyzed in a few minutes. It is fundamentally identical to the common pH measurement technique, an operator not conversant with electrochemical methods can find it simple to use. Analysis can be performed anywhere on site, since the electrode and pH-meter or Ion-analyzer are portable.

LIMITATIONS

The chloride ion selective electrode is limited in its use in organic solutions. Therefore, it is recommended that only 10% (v/v) hydraulic fluid (ehtylene glycol) solutions be used for analysis. The electrode must not stay in the solution for more than 2 minutes, and it must be cleaned thoroughly after every measurement. If the electrode is left for 3-5 minute duration in a hydraulic fluid solution its membrane will be damaged. If the cleaning procedure (recommended by the manufacturer) does not give reproducible results, it is better to replace the electrode.

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TABLE 1 - Chloride in water and ethylene glycol

Chloride, mg/L	Potential measurements in water		Potential measurements in 10% (v/v) ethylene glycol	
	No ISA added	ISA added	No ISA added	ISA added
0	251.6 mv	266.5 mv	231.0 mv	256.0 mv
1	243.0 mv	247.4 mv	224.9 mv	230.5 mv
10	184.5 mv	188.3 mv	169.5 mv	175.0 mv
100	125.5 mv	129.1 mv	113.6 mv	119.4 mv
1000	66.6 mv	70.2 mv	58.2 mv	64.8 mv

TABLE 2 - Effect of copper concentration on chloride measurements

Chloride, mg/L	Potential in 1% copper	Potential in 1% copper & 2mL ISA	Potential in 1% copper & 1% acid	Potential in 1% copper, 2mL ISA & 1% acid	Potential in 2% copper & 2 mL ISA	Potential in 2% copper & 1% acid	Potential in 2% copper, 2mL ISA & 1% acid
2	235.4	235.8	236.4	241.4	231.0	233.0	235.4
10	186.0	187.6	183.9	186.0	171.0	181.0	186.0
100	129.5	131.3	131.0	129.5	145.0	125.0	129.5
1000	78.0	79.0	74.3	74.3	69.4	73.2	78.0

TABLE 3 - Effect of copper on chloride measurements

Chloride, mg/L	Potential in 5% copper,	Potential in 5% copper & 1% acid,	Potential in 5% copper, 1% acid & 2 mL ISA	Potential in 10% copper,	Potential in 10% copper & 1% acid,	Potential in 10% copper, 1% acid & 2 mL ISA
	mv	mv	mv	mv	mv	mv
1	240.0	230.5	232.0	238.0	232.0	242.0
10	190.0	185.0	187.0	190.0	186.0	188.0
100	135.0	130.2	130.0	137.0	134.0	130.0
1000	83.0	79.0	80.0	82.0	78.0	84.0

TABLE 4 - Chloride in hydraulic fluids

Sample MIL-H-5559	Chloride, mg/L Direct analysis	Total chloride, mg/L Standard addition	Chloride, mg/L Actual amount present
S 1	2.5	12.52	2.52
S 2	2.7	12.75	2.75
S 3	4.28	14.30	4.30
S 4	4.25	14.31	4.31
Residue S 1	0.0	10.01	0.01
Residue S 2	0.0	10.0	0.0
Residue S 3	0.0	10.02	0.02
Residue S 4	0.02	10.0	0.0

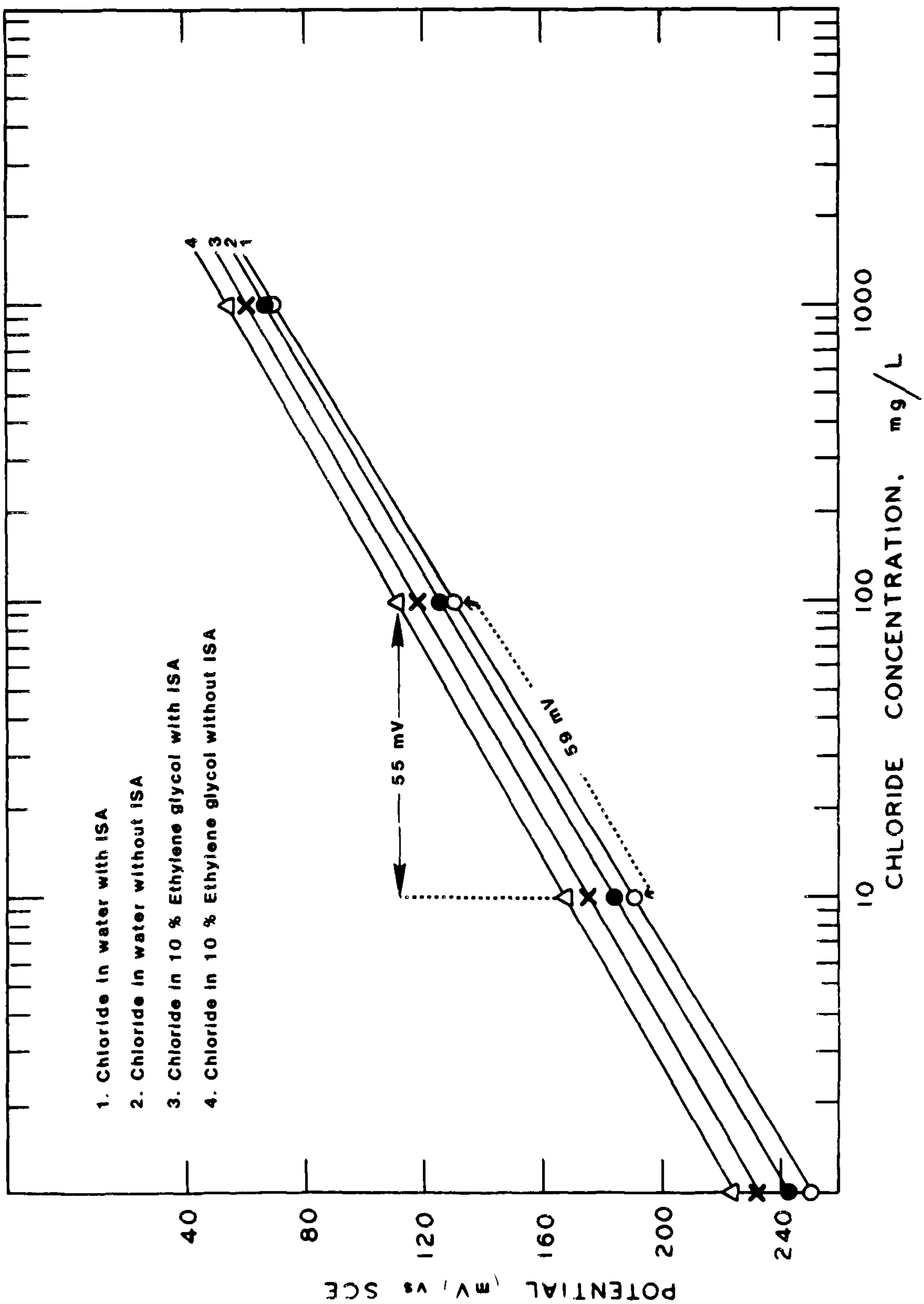

Figure 1. Calibration Curve for Chloride

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